

Low Stress Films of Cyclic Polybutadiene-Diurethanes by Vacuum Annealing

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We report here a vacuum annealing technique for the post-deposition processing of crystallized polybutadiene diacetate (CBDA) films. The technique has proven effective in reducing film stress from 3.1 ± 0.5 to 0.7 (in Dynes/cm 2) when the material is annealed at 1.4 ± 0.2 x 10 3 dynes/cm 2 . The reduction in stress is due to a net reduction in Δ under birefringence by a factor of two. This reduction in stress birefringence is important in the building of multilevel metallization structures where problems associated with patterning of films and automatic wafer handling equipment are encountered with initially bowed substrates. A change in the glass transition temperature from -130 to -175 °C was also observed in the vacuum treated films and mechanical compliance in the substrate was seen to occur at -175 °C instead of -130 .

We report here on a new vacuum curing technique for the post-deposition processing of a cyclized polybenzocyclobutenes rubber photocurable ISR, CRB-IRG01. This method has proved to be effective in reducing film stress and water loss. The effect of the curing method on other mechanical properties of this material will also be discussed.

КАПИТАЛ

Low density (LD) crystallized polybutadiene rubber photocatalysts having an average molecular weight (M_w) of 4.3×10^5 and a polydispersity (P_w/P_n) value of 8.20 were obtained from B.F. Goodrich Co., Inc. A medium grade styrene was used to further dilute the material. Water, 30 mM thioctic acid, and 4 mM diamine were added to further dilute the material. In order to calculate film areas the water layer was measured with the substrates either room temperature or 40°C . Copper coated Cu-foils were used to obtain as standing films for measurements of dynamic Young's modulus as a function of temperature. Quartz and sapphire (Al_2O_3) wafers nominally 520 μm thick and 100 μm diameter were used to measure areas as a function of temperature.

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Specimen Preparation The samples were cut from the 10 mm thick were spray coated with a 20 nm film thickness by using the spray coating technique. Film 10 nm thick were obtained (i.e., water bow

Low Stress Films of Cyclized Polybutadiene Dielectrics by Vacuum Annealing

Polymer dielectric materials play a significant role as interlayer insulators in multilayered crystallized-chain polymers for VLSI. Among them, crystallized polybutadiene rubber (CBR), has shown the greatest potential because of its relatively low dielectric constant (2.6), high thermal stability (-300°C) and ease of processing.¹ Unfortunately, like most polymeric materials, CBR exhibits large hysteresis after thermal cycling at high temperatures. This stress results mainly from the thermal expansion of the polymer chains which occurs during the crystallization and polymerization process. The stress can also be due to the shrinkage of the polymer chains and solvent removal. Excessive stress can lead to film delamination, cracks in the polymer film and ultimate failure.

INTRODUCTION

Polymer dielectric materials play a significant role as interlayer insulation in multilayer metalization techniques (see VI-5). Among them, cyclized polybutadiene rubber (CBR), has shown great potential because of its relatively low dielectric constants (2.6), high thermal stability (-300°C) and ease of processing.¹ Unfortunately, the most polymeric materials, such as CBR deposited on Si wafer develop stress after thermal cycling at high temperatures ($>200^\circ\text{C}$).² This stress results mainly from the thermal expansion of the substrate and polymeric material, but it is also due to the shrinkage which occurs during oxygen and solvent removal. Excessive stress can lead to film delamination, cracks in the polymeric film and substrate bow.

Chemical modification of polymers which leads to reduced stress has already been achieved with some polyesters but these are not as yet commercially available. Positive separation processing techniques have been previously used to control stress in borgage areas. However, we do not know of any current methods that have been developed to reduce stress in opposite directions [11a].

We report here on a new vacuum curing technique for the post-curing processing of uncrosslinked polybutadiene rubber photocatalyst (SR, CRB-MPQ). This method has proved to be effective in reducing film stress and water bow. The effect of the curing method on other mechanical properties of this material will also be discussed.

КАПИТАЛ

Low viscosity ($[\eta] = 0.5$ cP) crystallized polybutadiene rubber photomask having an average molecular weight (M_w) of 3.2×10^6 and a polydispersity (M_w/M_n) value of 8.20 was obtained from SR of America, Inc. ACS reagent grade styrene was used to further dilute the material. In water 20 mil thick and 4 inch diameter of $\langle 100 \rangle$ crystal orientation were used as the substrate. In order to calculate film stress the water base was measured with the substrates at either room temperature or 40°C . Copper coated Si wafers were used to obtain standard films for measurements of dynamic Young's modulus as a function of temperature. Quartz and sapphirine (Al_2O_3) wafers nominally 520 μm thick and 100 mm diameter were used to measure stress as a function of temperature.

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and the rubberized asphalt were characterized (i.e., water absorption measured) by laser diffraction techniques. Films 10 microns thick were spray coated onto 2-tonne concrete slabs in polyurethane coatings. Coatings 100 microns thick were sprayed onto 100-mm diameter cylindrical specimens. The Cycolane rubber was supplied by Ameron International Corporation to Lane Guttery Coatings Systems Model 10,000. The Cycolane rubber was obtained by addition 50 ml of styrene to 100 ml of monomer.

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parameters needed to obtain the desired 10 μm thickness are listed in Table I. Before proceeding the film, it was necessary to allow the solvent sufficient to evaporate for 5-10 minutes while maintaining the substrate level in order to ensure sufficient film thickness. Pre-baking at 100°C in air for one hour using a hot plate. A Mallin Box Ovens Model B-122 was used to further extend the film.

In order to vacuum anneal the film, the oven was turned on to a setting of 200°C after the oven had first been connected to a gauge pressure reading of 27 inches of mercury. The oven was held at this 200°C setting for 60 minutes while the samples were heated. Due to the thermal lag of the oven, this resulted in an effective baking time of only 30-45 minutes at 200°C. After the vacuum curing step was completed the oven chamber was backfilled with nitrogen gas flows at ~260 ml/min. This heating was maintained for 90 minutes to give an effective cure of 10-15 minutes at 200°C. The samples were then allowed to cool under a N_2 recommended process from the manufacturer. This process consists of first heating the film at 200°C in air for 30 minutes then heating at 200°C in N_2 for 30 minutes.

Free standing films needed to measure dynamic mechanical properties were obtained using 300A Cu/250A Cr film patterned on Si. The substrate (6 inch wafers) were first spray coated with the CBR and then put through the annealing process described above. The metal film containing the polymer layer was readily peeled off the Si surface and etched away using a potassium ferricyanide solution. Low dose刻離 dose ablates were required to completely remove the metal to give free standing film of the polymer.

Dynamic mechanical properties were measured using a Rheometrics Model DDV-II made by Toyo Instrument Company, Tokyo, Japan. The dynamic Young's modulus of the sample was measured in N_2 from 20 to 400°C at a rate of about 2°C/min, and a frequency of 110 Hz.

RESULTS AND DISCUSSION

After the thermal cycle the manufacturer's suggested annealing process resulted in a film stress at room temperature of $3.1 \pm 0.5 \times 10^6$ dyn/cm² (results) and a water bow of about 3.9 mm for 10 μm thick film. Using the vacuum annealing process described above the film stress measured $1.4 \pm 0.2 \times 10^6$ dyn/cm² and the water bow was about 1.9 μm for 10 μm thick film. This represents a 50% reduction in film stress and water bow by a factor of three and two respectively.

Dynamic mechanical data (Figure 1) show that vacuum annealed films have slightly smaller in phase moduli, E' , (2.3×10^6 dyn/cm²) than those annealed by the manufacturer's recommended curing process (2.1×10^6 dyn/cm²). However, the glass transition plot is seen to change from $\sim 320^\circ\text{C}$ to $\sim 130^\circ\text{C}$. Also, film annealed at 200°C were found to be very brittle, whereas those annealed in air were very brittle. This clearly indicates that a much more amorphous material (with a different micro-environment due to more complete solvent removal) results from the vacuum annealing process.

Figure 2. Using the three substrates above via bare thermal expansion coefficient (TEC) it was possible to deduce the relative TEC value for CBR. For the temperature range studied the TEC for CBR was consistently greater than that for graphite ($7.4 \times 10^{-6}\text{ }^\circ\text{C}^{-1}$) and had a stress value of 13×10^6 dyn/cm². However, the strain-temperature curves were found to be non-linear in the temperature regime below 200°C. This anomalous behavior was as unexpected given that organic and inorganic films normally show a linear relationship between stress and temperature.¹ One possible explanation for this is the low T_g of the vacuum annealed CBR film which becomes rubbery as the temperature approaches T_g during the heat relaxation should bring about a progressive larger decrease of film stress. The in situ stress measurements also show that mechanical coupling to the substrate (as indicated by zero

stress) occurs at $\sim 130^\circ\text{C}$ for the vacuum annealed film. These films also showed no hysteresis in room temperature stress following repetition of the annealing process. Films of CBR on Si substrates which did not undergo vacuum annealing (dashed curve Figure 2) did show a linear dependence of stress as a function of temperature. However, in this case mechanical coupling to the substrate occurred at $\sim 280^\circ\text{C}$ (extrapolated value) and a hysteresis in room temperature stress ($\sim 20\%$ increase) was observed. We were unable to measure stress levels above 200°C because CBR will oxidize when heated in air above this temperature for prolonged periods of time and the equipment was not available to carry out experiments at high temperatures in an inert atmosphere.

Table II summarizes the differences in mechanical properties of films of CBR annealed using the manufacturer's recommended process vs. those annealed under vacuum. The physical reactions that occur during the annealing process are not known. However, since the thermal treatment is essentially the same for both types of surfaces except for the environment to which they are exposed at 200°C , it may be suggested that the films prepared according to the manufacturer's suggested annealing process had undergone extensive crystallization as a result of their exposure to air at 200°C . Some oxidation may have also occurred and it is studies to investigate this possibility are under current investigation. Future work will be directed at clarifying the cause for the reduction in film stress and finding ways to improve the results. Preliminary experiments using other techniques consisting of higher vacuum soak times at 200°C or vacuum annealing at high temperatures have not proven successful in further reducing film stress.

SUMMARY AND CONCLUSION

We have described a vacuum annealing technique for CBR films which effectively results in a reduction of stress by a factor of three. Obviously, when the final annealing temperature is the same as that employed in the manufacturer's recommended process, the films can be said to have been cured to the same extent, yet they show different mechanical properties. A detailed explanation for these differences is yet to be determined. However, this change in the mechanical properties is beneficial in that the net result is a reduction in wafer bow by a factor of two.² This is very important to the manufacture of devices where problems with patterns of film and automatic wafer handling equipment are encountered with extensively bowed substrates.

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TABLE I

MATERIAL PRESSURE (IN. OF WATER)	50
ATOMIZATION PRESSURE (IN. OF WATER)	15
TRAVESE SPEED (IN./S)	16
CONVEYOR SPEED (IN. PER SPRAY STROKE)	1/2
SPRAY GUN HEIGHT (IN.)	6.5
NOZZLE DIAMETER (mm)	0.5
SPREADER TYPE	RBS

TABLE I. Spray deposition parameters needed to obtain good CBR 3000 film 10 μm thick.

TABLE II

MECHANICAL PROPERTY	NO VACUUM	VACUUM ANNEALED
STRESS (dynes/cm ²)	$3.1 \pm 0.5 \times 10^8$	$1.4 \pm 0.2 \times 10^8$
WAFER BOW (10 μm THICK FILM)	$\approx 39 \mu\text{m}$	$\approx 19 \mu\text{m}$
DYNAMIC VISCOELASTICITY,		
IN-PHASE MODULUS (110 Hz) (dynes/cm ²)	2.9×10^{10}	2.3×10^{10}
T_g	$\approx 320^\circ\text{C}$	$\approx 130^\circ\text{C}$
TOUGHNESS (FREE FILM)	BRITTLE	PLIABLE
MODULUS VS TEMP (125 - 200°C)	\approx LINEAR	NON-LINEAR
STRESS VS TEMP (225 - 200°C)	\approx LINEAR	NON-LINEAR

TABLE II. Comparative mechanical properties of CBR film annealed per manufacturer's assigned process (no vacuum) vs. those annealed in vacuum.

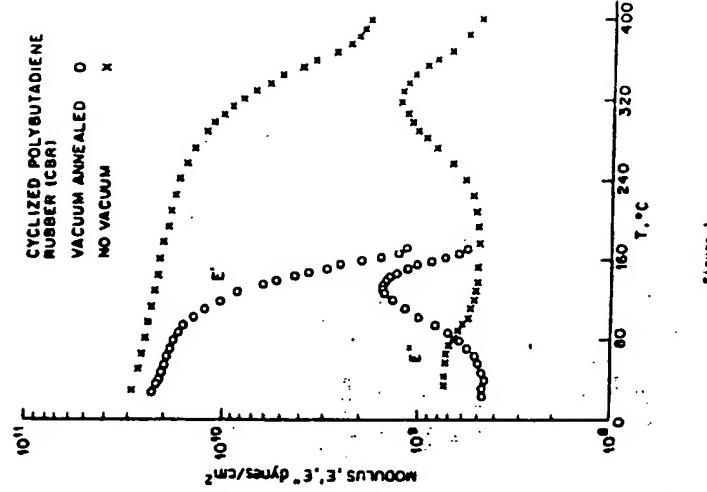


Figure 1

Figure 1. Dynamic mechanical properties of CBR-MP01 film. Vacuum annealed process (o), film annealed per manufacturer's assigned process (x).

PROCESSING CONCERNS FOR MULTI-LEVEL THIN FILM METALLIZATION

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ABSTRACT

Evaporation of multi-layer metallic thin film structures, bearing reactive metals like Ti, requires good control over the metallization process. During sequential deposition, the delay between the deposition of Ti and the next layer (X) and the pressure in the evaporation chamber during metallization, determine the impurity contents at the Ti/X interface which in turn influences the electrical and mechanical properties of the structure. If the starting pressures of Ti and X is less than 3×10^{-4} Pa and the delay between the deposition of structure is low and is process independent. The mechanical strength of the structure is, however, more sensitive to contamination at the Ti/X interface. The use of multiple electron gun systems to eliminate delay during deposition and the practice of pre-evaporating Ti, to clean the chamber prior to evaporating the thin film structure, will ensure electrically and mechanically sound structures.

INTRODUCTION

Multi-layer metallic structures are becoming increasingly important in the electronics industry. To produce good multi-layer thin films, metallization techniques like evaporation have to be well understood and controlled. During the fabrication of thin film structures containing reactive metals like Cr, Zr or Ti, improper evaporation practice can lead to the contamination/oxidation of the reactive surfaces, which in turn will degrade the performance of the structure. Kemmerer and Mills [1] have shown that Ti/Cu interfaces delaminate if processing chamber pressures are not carefully controlled. If contamination at the interface is not adequate to cause delamination of the

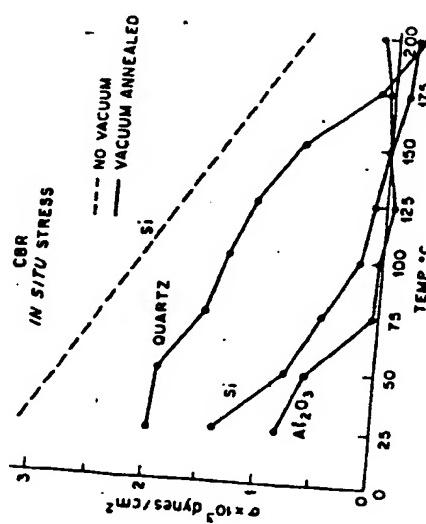


Figure 2

Figure 2. Stress-temperature measurements of vacuum annealed CBR-M491 films (solid line) and film cured using the manufacturer's suggested annealing process (dashed line).